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Radiation Dosimetry in Relation to High Intensity Radiation Sources

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A dosimeter suitable for measuring the radiation intensity at doses in the range of 10^4 to 8×10^5 rads consists of a solution of 0.001M ferrous sulfate-0.01M cupric sulfate in 0.010N sulfuric acid. If the recommended concentrations are used, the dosimeter is reproducible to $\pm 0.3\%$ and stable after irradiation to approximately 2% per week. The dose received by the recommended dosimeter can be calculated, if read at 25°C., by converting the change in absorbance (ΔA) using the equation: dose (rads) = $\Delta A \times 6.43 \times 10^5$. This solution may be stabilized against thermal changes by preirradiating the solution to approximately 10^5 rads. This solution is then stable, changing approximately 2% per week.

The Fricke dosimeter (ferrous sulfate solutions) has been used to measure the radiation intensity of various types of ionizing radiation sources since its development by Fricke and Morse in 1927 (2). It is widely accepted because it yields accurate and reproducible results with a minimum of care. This system meets many of the requirements specified for an ideal dosimeter (5, 9); however, it has a limited dose range, and for our applications it has been necessary to develop a dosimeter covering larger doses. Of the systems reviewed (6, 7), two (ferrous sulfate-cupric sulfate and ceric sulfate) showed the most promise for use with the radiation sources at the U. S. Army Natick Laboratories (8). Of these, the ferrous-cupric system has received the most use, and this paper describes our experience in using this system and suggests procedures by which it may be used by others with equal success.

The standard ferrous-cupric dosimeter as described in the literature (3, 4) consists of an air-saturated solution containing 0.001M FeSO_4 , 0.010M CuSO_4 , and 0.010N H_2SO_4 . If prepared fresh daily, this solution is suitable for measuring doses in the range of 10^4 to 8.0×10^5 rads. Under controlled conditions, this system is reproducible to within 1%. A slight increase ($\pm 1\%$) in the uncertainty occurs as a result of batchwise variation. Com-

parison of each new batch against a standard—e.g., a Fricke dosimeter—is, however, not required for reproducible results.

The above solution may be stabilized against thermal changes by pre-irradiating it to approximately 10^5 rads with ionizing radiation. This solution is then stable, changing approximately 2% per week.

The upper dose limit may be extended to more than 3×10^6 rads by increasing the ferrous ion concentration from 0.001M to 0.01M. The range may be increased if the ferrous concentration is further increased (9).

Experimental Procedure

Ferrous sulfate-cupric sulfate solutions are prepared, varying the range of each between 0.0001 and 0.1M by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Baker analyzed), and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Fisher certified) in H_2SO_4 (Baker and Adamson) and diluting with distilled water (Barnstead single distilled).

Irradiations are carried out in Kimax glass ampoules. These ampoules are filled with 5 cc. of the solution, irradiated, using the apparatus previously described (7), and flame-sealed with a Perfe Keum Model HS-1 ampoule sealer. The irradiation source used for these experiments is a 1.3×10^6 curie cobalt-60 source consisting of two parallel plaques 56 inches wide by 48 inches high, spaced 16 inches apart. For most irradiations, the ampoules are placed in the center of a Masonite phantom which completely fills a No. 10 can (6 inches in diameter by 7 inches high). The can is placed in a fixed position in an aluminum carrier and transported into the irradiation cell to a predetermined position (5). The source is then elevated from the bottom of a 25-foot, water-filled pool into the irradiation position. After the desired exposure, the source is lowered to the bottom of the pool.

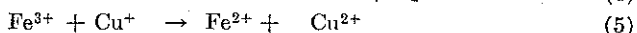
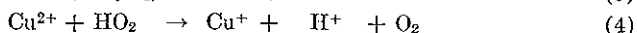
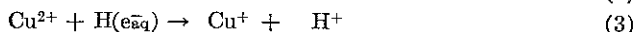
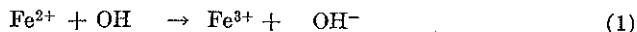
The time required to raise or lower the source is 1.5 minutes, comparable to an irradiation dose in the irradiation position of approximately 35,000 rads (transient dose). The dose rate in the irradiation position is approximately 60,000 rads per minute. Calibration of the ferrous-cupric dosimeter is determined by comparison with the Fricke dosimeter, when irradiated at a position in the cell having a lower dose rate. The dose rate in the calibration position is approximately 5×10^3 rads per minute with a transient dose of approximately 3×10^3 rads. Calibrations made at such a position when using a $G(\text{Fe}^{3+}) = 15.6$ for the Fricke dosimeter gave a $G(\text{Fe}^{3+})$ of 0.66 for the ferrous-copper dosimeter.

The ferric ion concentrations are determined by measuring the absorbance of the solutions, using a temperature-controlled (25°C.) spectrophotometer with the absorption peak around 304 m μ . It is necessary to measure the extinction coefficient at the absorption peak for each instrument used. The molar extinction coefficients for our instruments are 2200 for the Cary model 15 at 302.5 m μ and 2352 for the Beckman model DB at 304 m μ .

Chemistry

It has been established (3, 4) that by adding cupric sulfate to modify the Fricke dosimeter, it is possible to reduce the $G(\text{Fe}^{3+})$ drastically from 15.6 to 0.66.

The effect of the cupric sulfate is revealed by the following reactions (1):



Since oxygen is not consumed in the over-all reaction, it does not affect $G(\text{Fe}^{3+})$. This dosimeter shows no dose rate effect under the usual conditions of γ -ray irradiation since all of the above reactions except Reaction 6 are fast, and this reaction has a half-life of 14 seconds in 0.001M ferrous sulfate (1).

Experimental Results

When a system is being considered as a routine dosimeter, it is desirable to investigate the effect of altering various parameters—e.g., acid concentrations, reagent concentrations, and storage time—on the results obtained. To obtain this information, a series of experiments was conducted.

Effect of Acid Concentration. Figure 1 shows the effect of changing the acid concentration in a solution containing 0.01M copper sulfate and 0.001M ferrous sulfate. Minor variations in the acid concentration (0.01N \pm 0.005N) result in a variation of less than 5% in the G value. These

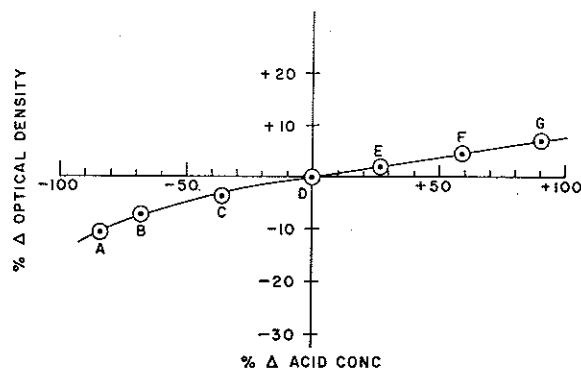


Figure 1. Effect of initial sulfuric acid concentration on ferric ion yield (ΔA), measured after irradiating of standard ferrous-cupric dosimeter to approximately 400,000 rads

M 1.0.84N H_2SO_4 per 1000 ml.	
A. 2	E. 16
B. 4	F. 20
C. 8	G. 24
D. 12.6	

solutions were prepared by adding various volumes of 0.8N H_2SO_4 to pre-weighed salts of ferrous and cupric sulfate and then diluting to volumes with singly distilled water. Figure 2 shows the linear relationship of the change in absorbance of the irradiated solution as a function of irradiation exposure time (or radiation dose). Although the slopes of the curves for various solutions are similar, their apparent transient dose is different (35,000 and 76,000 rads). This could cause difficulties in using the system if the dose rate and transient doses are obtained by making a series of exposures for various times—e.g., 3, 5, 9, and 12 minutes—and then using the Y -intercept as the transient dose and the slope as the dose rate as described by Holm and Jarrett (5).

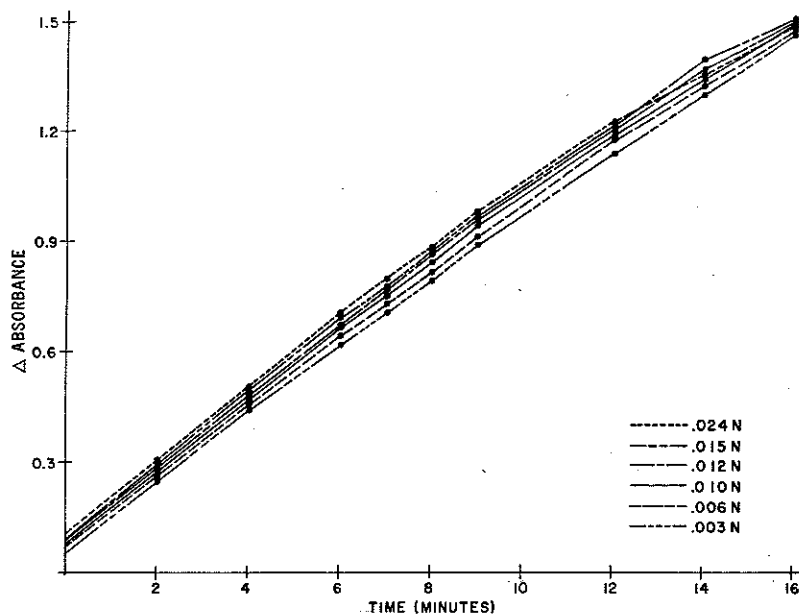


Figure 2. Effect of initial sulfuric acid concentration on apparent transient dose, as determined by Y intercept

Effect of Ferrous Ion Concentration. The reactions involved in the ferrous-cupric dosimeter, as described by Hart (1), are independent of oxygen concentration, and one would not expect to observe a change in the ferric yield $G(\text{Fe}^{3+})$ in this system when increasing the dose, as occurs in the Fricke dosimeter. This would indicate that the dose limit of this dosimeter is a function of the initial ferrous ion concentration and is not influenced by the oxygen concentration. To explore this idea, we increased the ferrous ion concentration from 0.001M to 0.01M while keeping the

other components constant. As seen in Figure 3, the linear measuring range of this dosimeter is in fact increased beyond the 3-megarad limit of this experiment. This response has not as yet been explored completely and is the subject of a current study. The indications are that by increasing ferrous ion concentration and preirradiating the solutions, a usable system may be developed to compete with the ceric sulfate dosimeter in the range 10^4 – 10^8 rads. Obviously, when higher ferrous ion concentrations and higher doses are used, readings can no longer be obtained directly from spectrophotometer; the solution must be diluted with sulfuric acid before reading. This additional inconvenience can be more than compensated by the fact that the system may be considered as a secondary standard not requiring recalibration of each new batch of the solution against a standard such as the Fricke dosimeter, as is now required by the ceric system.

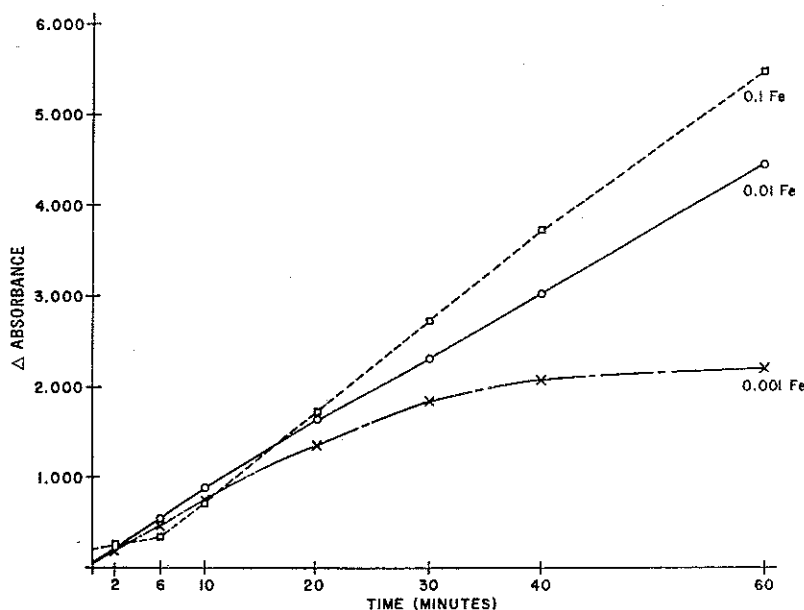


Figure 3. Effect of initial ferrous ion concentration on linear portion of absorbance-irradiation time (dose) relationship

Effect of Cupric Concentration. The cupric ion concentration was varied between $0.0001M$ and $0.1M$ to determine its effect on the "standard" ferrous copper dosimeter. Figure 4 shows that as the cupric ion concentration is increased, the $G(Fe^{3+})$ decreases. A change of $\pm 0.005M$ from an initial cupric ion concentration of $0.01M$ results in a $\pm 10\%$ variation in the ferric yield.

Reproducibility. To determine the maximum variation in results that one might expect when using the ferrous sulfate-cupric sulfate system as a routine dosimeter, we prepared a number of dosimeters containing the standard solution and irradiated them in a No. 10 can similar to that previously described. These dosimeters gave a dose rate for the position of

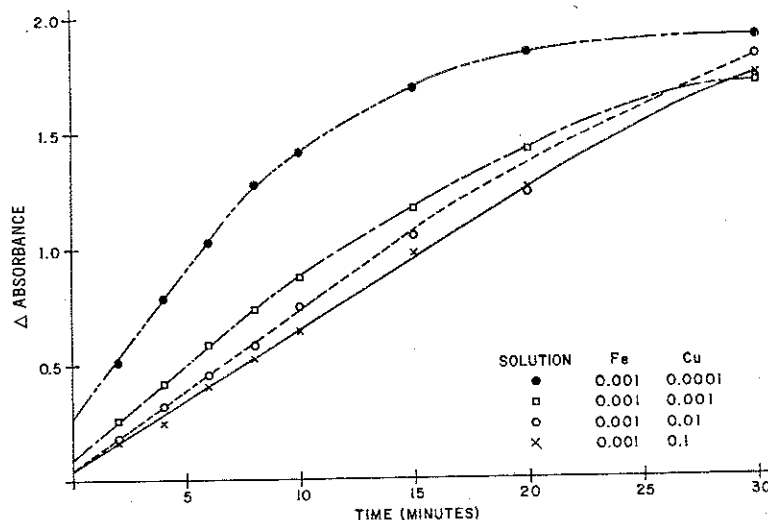


Figure 4. Relation of dose to absorbance curve of various initial cupric ion concentrations

$3.83 \pm 0.012 \times 10^5$ rads per minute or a reproducibility of $\pm 0.3\%$. Although this experiment was conducted under controlled conditions, variations between different solutions prepared by various experimenters did not exceed $\pm 1\%$. These solutions were prepared using reagent grade reagents and singly distilled water.

Storage Stability. The ferrous-cupric dosimeter has never received much attention as a dosimetry system because the unirradiated solution undergoes rather rapid changes during storage (Figure 5). To solve this problem, our first approach was to read the unirradiated (blank) solution against distilled water at the start of irradiation, then read all irradiated solutions against a distilled water blank rather than the unirradiated blank, and, finally, to subtract the two to obtain the change in absorbance. This procedure can be successful, provided the dose rate of the radiation source is relatively high or corrections are made for this autoxidation. Figure 6 shows that after the solution has been irradiated to an absorbance greater than 0.2, the change in absorbance with time is relatively stable (within 2% per week).

If the change in absorbance is made by comparing the irradiated with the unirradiated solution by using the unirradiated solution as the blank,

the results will vary as a function of the time elapsed between the start of irradiation and the time at which the samples are read. This variation can lead to large errors. However, the stability of solutions irradiated in excess of 10^5 rads indicates that this provides a method of stabilizing the solution before use as a dosimeter. We have evaluated this technique for the standard ferrous-copper dosimeter and found it to be useful. Figure 7 shows the linearity of the change in absorbance *vs.* dose. This technique lowers the range of the dosimeter but provides a stable system. By increasing the ferrous ion concentration, it should be possible to overcome the disadvantage of lowered range.

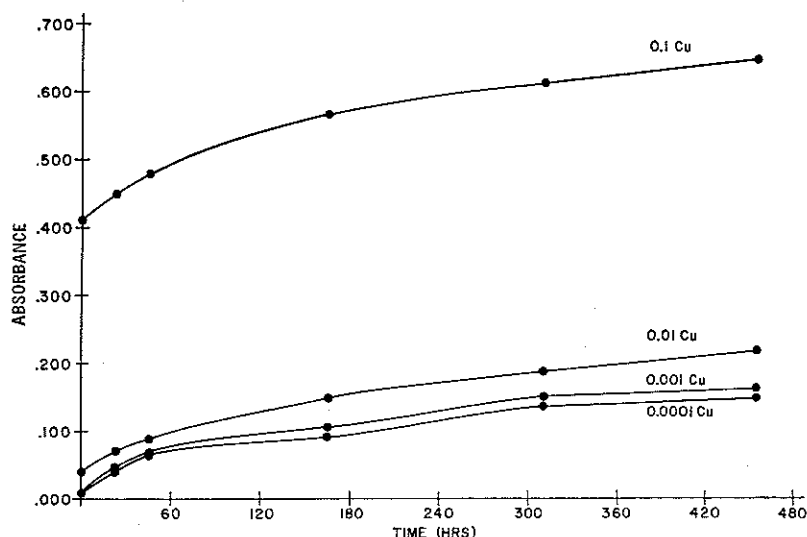


Figure 5. Storage stability of unirradiated ferric cupric solutions of varying cupric ion concentrations

Effect of Temperature during Reading. The molar extinction coefficient of Fe^{3+} was determined temperature-dependent in the temperature range 20° – 55°C . to the extent of 0.59% per degree centigrade. It is, therefore, necessary to read the solutions in a temperature-controlled spectrophotometer or to correct for the temperature variation for 25°C .

Discussion

There is no question that the ferrous-cupric dosimeter can be used for routine dose measurements if the unirradiated solution is read at the start of the irradiation and not used as a blank against which the irradiated solutions are compared. The irradiated solutions can be held up to 1 month before reading without affecting the results by more than 10%. If it is inconvenient to prepare the solution fresh before each day of irradiation, the

old solutions can be used, provided a blank is read before the start of irradiation; alternatively, the solution can be stabilized by irradiating it so that it has an absorbance greater than 0.2 (approximately 10^5 rads). Pre-irradiation reduces the useful range of the standard dosimeter, but may not be a problem if the ferrous ion concentration is increased to 0.01M.

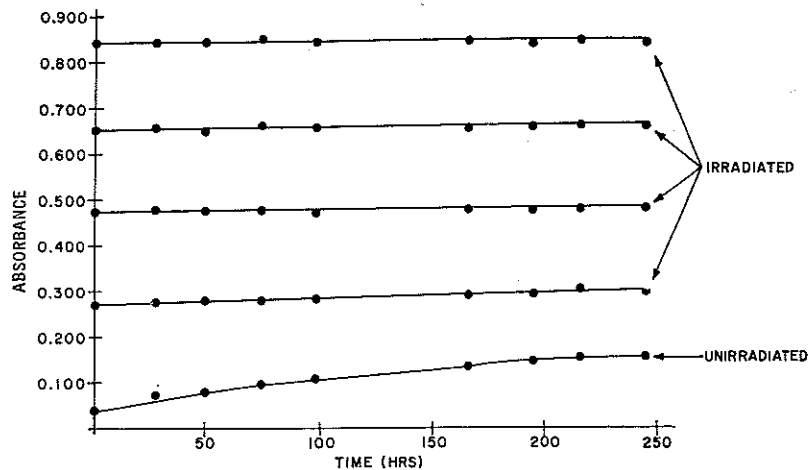


Figure 6. Storage stability of standard ferrous-cupric dosimeter, unirradiated and irradiated, to various initial absorbances
Ferric ion concentration

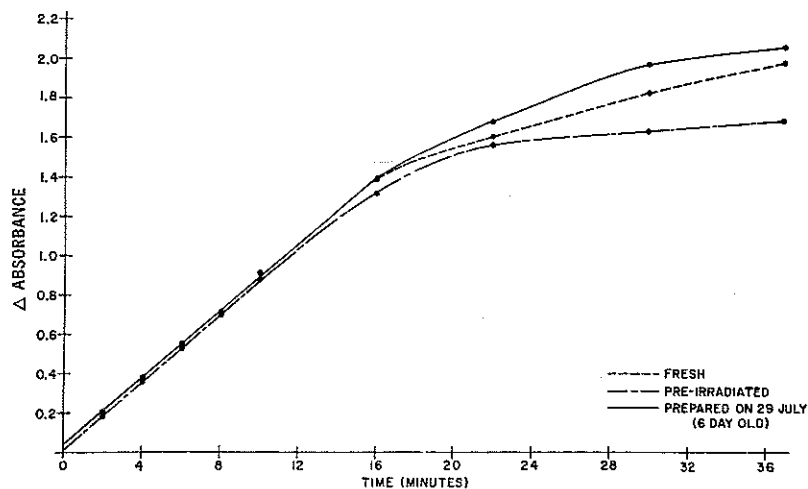


Figure 7. Relation of irradiation time to absorbance curves for fresh preirradiated and stored solutions of standard ferrous-cupric dosimeter

For routine use, the dose the standard ferrous-cupric dosimeter (0.001M FeSO₄, 0.01M CuSO₄, in 0.01N H₂SO₄) has received can be calculated, if read at 25°C., from the following equation:

$$\text{Dose (rads)} = (A_i - A_u) \times 6.43 \times 10^5$$

where A_i = absorbance of irradiation solution

A_u = absorbance of unirradiated solution

6.43×10^5 = constant value assuming a G value of 0.66, molar extinction coefficient of 2200 at 25°C., density of 1.024, and unit conversion factors.

A correction of 0.59%/°C. must be made for the absorbances if the solution is read at a temperature other than 25°C.

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Literature Cited

- (1) Fricke, H., Hart, E. J., "Radiation Dosimetry," F. Attix and W. Roesch, eds., Vol. 2, p. 167, Academic Press, New York, 1967.
- (2) Fricke, H., Morse, S., *Am. J. Roentgenol.* 18, 430 (1927).
- (3) Hart, E. J., *Radiation Res.* 2, 33 (1955).
- (4) Hart, E. J., Walsh, P. D., *Radiation Res.* 1, 342 (1959).
- (5) Holm, N. W., Jarrett, R. D., "Evaluation of Dosimetry Procedures Applicable for Use in Food Irradiation," Radiation Preservation of Foods, p. 361, National Academy of Sciences, National Research Council, 1965.
- (6) Jarrett, R. D., "Dosimetry and Dose Distribution," Eighth Contractors' Meeting, Radiation Preservation of Food Program, PB 166166 (1964).
- (7) Jarrett, R. D., Halliday, J. W., "Dosimetry in Food Preservation by Ionizing Radiation," U. S. Army Natick Laboratories, R&D Associates Activities Report, Vol. 15, December 1963.
- (8) Mehrlich, F. P., *Food Processing, Packaging* 24 (5), 84 (1963).
- (9) Weiss, J., Allen, A. O., Schwartz, H. A., "Use of the Fricke Sulfate Dosimeter for Gamma Ray Doses in the Range 4 to 40 Kiloröntgen," Proceedings of First International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955, P/155, pp-14, 179.

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